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(54) Polyurethane sealant system and method of forming a high tensile strength seal on glass and/or metal.

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A polyurethane sealant includes a polyurethane having terminal isocyanate groups and a dual curing catalyst of an organic bismuth compound and an organic tin compound. The polyurethane is a reaction product of a liquid poly (lower)alkylene polyol having a molecular weight of 6,000 or more and three to five hydroxyl groups and a sterically unhindered aromatic diisocyanate. The polyurethane sealant may be used in conjunction with a silane based primer and when applied to glass surfaces provides a high strength and rapidly curing seal.

EP 0 040 469 A2

POLYURETHANE SEALANT SYSTEM AND METHOD OF FORMING A HIGH TENSILE STRENGTH SEAL ON GLASS AND/OR METAL

The present invention relates to a polyurethane sealant system and more particularly relates to a polyurethane sealant which when exposed to ambient moisture will cure rapidly to form a seal having high tensile strength and to its use for forming a high tensile seal on a glass or metal substrate.

Inasmuch as fast room temperature curing, single component sealants and adhesives are desirable and useful, particularly in original equipment manufacturing, it is not surprising that a number of one component elastomeric sealants are now available in the marketplace. Such sealants include various polymer bases such as polysulfides, mercaptan terminated polyethers, polysiloxanes and polyurethanes.

Certain industries need elastomeric adhesives or sealants which cure by exposure to ambient conditions and which will develop a high tensile strength. Applications of this type include sealing automobile windshields which are often intended as structural components in design. For such applications the elastomeric sealant or adhesive must not only have high tensile strength but should achieve such strength in a matter of a few hours so that the autombile may be safely driven shortly after installation of the windshield.

Of the various liquid elastomers available today, cured polyurethanes, in general, have the highest mechanical strength and therefore are the polymers of choice as a windshield sealant or adhesive provided that the adhesive or sealant can cure rapidly under ambient conditions without exhibiting other problems such' a foaming, storage instability, depolymerization, etc.

An example of a one component, room temperature, moisture curing polyurethane sealant is disclosed in United States Patent No. 3,779,794 wherein a polyurethane sealant

in combination with a particular type of silane primer is disclosed. In that patent, the polyurethane sealant is an isocyanate terminated polyethylene ether diol-polypropylene ether triol combination having from 1.2 to 1.5% free isocyanate terminals. These terminals are blocked with a volatile blocking agent which, when exposed to air, evaporates, and the moisture in the air cures the polyurethane. The polyurethane sealant disclosed in this particular US Patent in combination with the silane primer cures, according to the patent, to a tensile strength of 2.81-4.22 kg/cm^2 (40-60 pounds per square inch [psi]) after 6 hours exposure at 25°C (77°F) and 30% relative humidity. Although such sealants are satisfactory in terms of ultimate elongation characteristics and the like, nevertheless, there is a need for the development of a sealant having higher early strength, i.e. 7.03 kg/cm^2 (100 psi) or more in a six hour period of time, with equivalent ultimate elongation.

Japanese Patent Application No. 1979-126297 (laid open 1979 October 01) relates to a urethane sealant formed from the reaction of an organic diisocyanate and a polyalkyl ether polyol. The urethane disclosed in this Japanese application preferably has a molecular weight between 5,000 and 6,000 and the isocyanate groups thereof are blocked with a volatile blocking agent such as dimethyl malonate. Catalysts for use in the curing of these urethanes as disclosed in the Japanese application are those which are common in the art. There is, however, no suggestion at all in the Japanese application of the use of a mixture of catalysts.

The present invention is based upon the surprising discovery that one component, room temperature curing, stable polyurethane sealants having extremely rapid cure rates and high early strengths are produced by incorporating a dual catalyst system of certain organic tin and bismuth salts in a polyurethane sealant produced by using sterically unhindered aromatic isocyanates to terminate liquid poly

(lower) alkylene ether polyols having functionalities between three to five (i.e. poly(lower)alkylene ethers with three to five terminal functional hydroxyl groups per molecule) and molecule weights above about 6,000 together with a volatile blocking agent to block the isocyanate groups. (As used herein and throughout the description, claims and abstract, the term "lower" when used in conjuction with the terms "alkyl" and "alkylene" means, respectively, alkyl groups having from 1 to 6 carbon atoms and alkylene groups having from 1 to 6 carbon atoms). It has been found that the use of two curing catalysts is critical since using only one does not give satisfactory results. The unexpected synergistic effect of using a catalyst mixture of certain organic tin and bismuth compounds means that a three-fold improvement in 6 hours ambient tensile strengths are found compared with those of US Patent No. 3,779,794.

The polyurethanes produced with the dual catalyst organic tin and bismuth salts have very high tensile strengths, i.e. 7.03 kg/cm^2 (100 psi) and greater, in six hours after exposure to ambient moisture and temperature. Because of the ultimate higher strength, the polyurethane sealants of the present invention allow higher extensions with plasticisers thereby reducing the cost and yet still meet all the ultimate performance characteristics of auto-mobile manufacturers such as elongation.

Accordingly, the present invention provides in one aspect a polyurethane sealant which when exposed to ambient moisture will cure rapidly to form a seal having high tensile strength, comprising:-

(A) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of the polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane polymer being the reaction product of (1) a liquid poly

(lower) alkylene ether polyol having a molecular weight of greater than about 6,000 and from three to five hydroxyl groups with (2) a sterically unhindered aromatic diisocyanate;

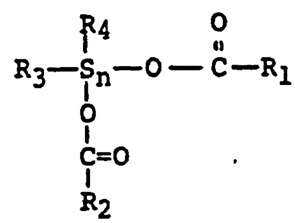
(B) a catalytic curing effective amount of a curing catalyst;

(C) up to 200 weight percent, based on the weight of the polyol, of inert fillers; and

(D) up to 100 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers, characterised in that the curing catalyst comprises:-

(a) an organic bismuth salt selected from bismuth tri-(2-ethyl hexoate) and bismuth tri-(neo-decanoate); and

(b) an organic tin compound of the formula



wherein R_1 and R_2 are the same or different and each is an alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl group.

In another aspect the present invention provides a polyurethane sealant system which when exposed to ambient moisture will cure rapidly to form a seal having high tensile strength, including:-

(A) a liquid polyurethane sealant comprising:-

(1) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of the polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane polymer being the reaction product of:-

(i) a liquid poly(lower)alkylene ether polyol having a molecular weight of greater than 6,000 and from

three to five hydroxyl groups with

(ii) a sterically unhindered diisocyanate;

(2) a catalytic curing effective amount of a curing catalyst;

(3) up to 200 weight percent, based on the weight of the polyol, of inert fillers;

(4) up to 50 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers; and

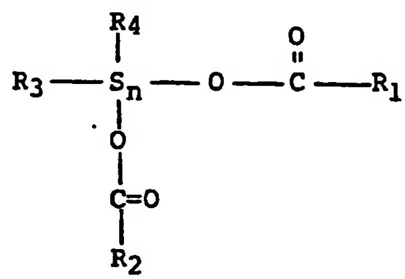
(B) a silane based primer composition which is rapidly curable in the presence of ambient moisture and comprising:-

(I) a silane compound having isocyanate reactive groups; and

(II) a catalytic effective amount of a silane hydrolysis catalyst; characterised in that the polyurethane curing catalyst comprises:-

(a) an organic bismuth salt selected from bismuth tri-(2-ethyl hexoate) and bismuth tri-(neo-decanoate); and

(b) an organic tin compound having the formula



wherein R_1 and R_2 are the same or different and each is an alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl group.

In a further aspect the present invention provides a method of forming a high tensile strength seal on a glass substrate which comprises priming the glass substrate which is exposed to ambient moisture with

(A) a silane based primer composition which is rapidly curable in the presence of ambient moisture and including:-

(1) a silane compound having isocyanate reactive

groups; and

(2) a catalytic effective amount of a silane hydrolysis catalyst; and then applying over said silane base primer

(B) a liquid polyurethane sealant comprising

(i) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of said polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane being the reaction product of:-

(a) a liquid poly(lower)alkylene ether polyol having three to five hydroxyl groups and a molecular weight of greater than about 6,000; and

(b) a sterically unhindered aromatic diisocyanate;

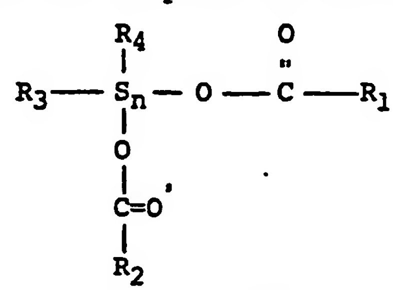
(ii) a catalytic curing effective amount of a curing catalyst;

(iii) up to 200 weight percent, based on the weight of the polyol of inert filler; and

(iv) up to 50 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers, characterised in that the curing catalyst comprises:-

(I) an organic bismuth compound selected from bismuth tri - (2-ethyl hexoate) and bismuth tri-neo-decanoate; and

(II) an organic tin compound of the formula



wherein R_1 and R_2 are the same or different and each is a lower alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl

group.

The polyurethane sealants of the present invention have a free isocyanate content of not more than about 2.0 weight percent and generally the sealants of the present invention will have a free isocyanate content of from about 0.5 weight percent to about 2 weight %.

The general procedure for producing the polyurethane sealant is to prepare a mixture of the polyol and any fillers and plasticisers. This mixture should be substantially free of moisture, e.g. the mixture should not contain more than about 0.06 weight % water. To this dry mixture is added the sterically unhindered aromatic diisocyanate and the tin catalyst, the amount of diisocyanate added being sufficient to react with all the hydroxyl groups present in the polyol and also any water residue present and having a free isocyanate content of not greater than about 2 weight %, for example from 0.5 to 2.0 weight % based on the weight of polyurethane polymer. The organic tin salt catalyst is added because in addition to promoting the curing of the polyurethane sealant upon exposure to moisture, it also promotes the reaction between the isocyanate and the hydroxyl groups. Thereafter, the free isocyanate groups are blocked by adding a volatile blocking agent in an amount about equal to, or slightly less than, the moles of free isocyanate in order to prevent further reaction of the isocyanate groups.

After the blocking reaction is completed, the organic bismuth salt catalyst is added in a catalytic effective amount. It is preferred to add the bismuth catalyst after the reaction between the polyol and diisocyanate has occurred.

As examples of the poly(lower) alkylene ether polyols useful in the present invention there may be mentioned poly(lower) alkylene ether triols, tetrols, pentols, and mixtures thereof. Preferred poly(lower)alkylene ether

polyols are polypropylene ether triols, tetrols, pentols, and mixtures thereof.

The poly(lower)alkylene polyols having three to five hydroxyl groups used in making the polyurethane sealants of the present invention are liquid and will have a molecular weight of 6,000 or greater. For example, the molecular weight may range from 6,000 to as high as 20,000 or 30,000 providing that the triol, tetrol, or pentol is liquid.

The polypropylene ether triols of the present invention are known in the art and therefore no detailed exemplification will be given herein. Such polypropylene ether triols may be made, for example, by the addition of propylene oxide to trimethylol propane or 1, 2, 6 hexane triol as disclosed in U.S. Patent No. 3,437,622.

The polypropylene ether tetrols and pentols used in the present invention may be made in the following manner: For the tetrol, two moles of polypropylene ether triol are reacted with one mole of a diisocyanate (either hindered or unhindered) such as tolylene diisocyanate by mixing the two reactants together followed by heating for 6 hours at 70°C. The pentol is made in the same manner by reacting three moles of the triol with two moles of the diisocyanate followed by heating.

The isocyanate which is reacted with the polyols to form the polyurethanes of the present invention may be any sterically unhindered aromatic diisocyanate, e.g. aromatic diisocyanates having no substituent on the aromatic ring which is ortho to either isocyanate group. (Toluene diisocyanate is not satisfactory since the methyl group hinders the final reactivity of the polymer). Exemplary of isocyanates useful in the present invention are diphenyl methane diisocyanate, biphenyl diisocyanate and diphenyl ethane diisocyanate. As noted above, it is important that enough isocyanate be utilised to have a free isocyanate content in the resulting completed sealants of not more than

2 weight %, preferably from about 0.5 weight % to 2 weight %.

As noted hereinabove, to prevent the free isocyanate groups from further reacting there is added a volatile blocking agent in an amount about equal to the equivalents of free isocyanate groups present. This volatile blocking agent is displaced by the ambient moisture during curing and therefore should be volatile at room temperature. These blocking agents are well known in the art and are described in detail in the following:-

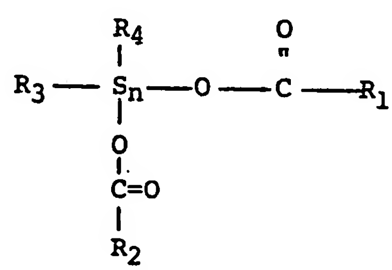
(1) S. Petersen, Annalen der Chemie, 562, 205 (1949)

(2) F. R. Griffin and L. J. Willworth, Ind. Eng. Chem. Proced. Res. Develop. 1, 265 (1962)

(3) Canadian Patent 722, 764 (Nov. 30, 1965)

Included are tautomeric enols such as di(lower) alkyl malonates.

In order to obtain high tensile strength rapidly upon exposure to moisture the polyurethanes of the present invention must contain a dual catalyst of organic tin and bismuth compounds. The organic tin compounds may have the following formula:-



wherein R_1 and R_2 are the same or different and each is an alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl group. Exemplary of such organic tin compounds are dibutyl tin dilaurate and dibutyl tin diacetate. The amount of organic tin compound present is not particularly critical

provided it is present in a catalytic curing effective amount which may generally vary from about 0.1 weight % to about 1 weight % based on the weight of the polyol.

The other compound of the dual catalyst is a bismuth organic compound such a bismuth tri - (2-ethyl hexoate) and bismuth (tri-neo-decanoate). As is the case with the organic tin compound, a catalytic curing effective amount must be present in the polyurethane which, for example, may vary from about 0.1 weight % to about 0.6 weight % calculated as bismuth and based on the weight of the polyol.

For maximum activity and reproducibility it is preferred that the organic tin salt of the dual catalyst be added after any pigments have been blended with the polyol and combined with diisocyanate. It has also been found beneficial to restrict the addition of the bismuth compound until completion of the isocyanate reaction and blocking of the free isocyanate groups with the volatile blocking agent.

It should be noted that the use of the two curing catalysts is critical in the present invention since the use of only one does not give satisfactory results regardless of the amounts used. Likewise the use of unhindered aromatic isocyanates is important in achieving extremely rapid cures. For example, when using only the organic tin compound, the polyurethane will have a tensile strength in six hours at 25°C (77°F) and 30% R.H. of about 3.5 kg/cm^2 (50 psi) and using only the bismuth compound results in a six hour tensile strength of about 2.11 kg/cm^2 (30 psi) with a resulting material having little elastomeric qualities. Surprisingly, when using the dual catalyst system, tensile strength well in excess of 7.03 kg/cm^2 (100 psi) regularly results after six hours cure. The polyurethane sealant also normally contains inert fillers and plasticisers so as to impart desired application and physical properties to the polyurethane composition. Inert fillers which may be used

in this invention are silicates, carbonates, such as calcium carbonate, and also carbon black. The fillers may be present in amounts of up to 200 weight %, for example, 50 weight % to 200 weight %, all such weight percentages being based upon the weight of the polyurethane.

The polyurethane sealants of the present invention also preferably contain a plasticiser which is inert to the isocyanate groups and compatible with the polyurethane. Such plasticisers are known in the art and include esters such as dioctyl phthalate, phosphates such as tricresyl phosphate, aromatic hydrocarbon oils and various chlorinated paraffins. The plasticiser may be present in amounts of up to 100 weight % based on the weight of the polyurethane.

The resulting polyurethane sealant may be used in conjunction with any silane based primer having isocyanate reactive groups so that the primer can react with the free isocyanate groups in the polyurethane sealant to form high strength, rapid curing seals between for example, glass and metallic surfaces. Isocyanate reactive groups include amine, epoxy, mercaptan, isocyanate and urea. Particularly preferred silane based primers having isocyanate reactive groups are the silane - isocyanate primers such as those disclosed in U.S. Patent No. 3,453,243. In this particular patent there are described primers which are the reaction product of an isocyanate with a silane and which contain isocyanate reactive groups. The particularly preferred silane based primer for use in the present invention is the reaction product of mercaptopropyl trimethoxy silane with 2, 2, 4-trimethyl hexamethylene diisocyanate. The primer composition of the present invention also preferably contains fillers such as carbon black and also are preferably dissolved in an organic solvent such as ethyl acetate or the like to form a dilute solution thereof. In addition, a film forming resin binder should desirably also be present, such resins being known in the art. For example, chlori-

nated rubber can be used such as those obtainable from ICI (e.g. Alloprene 4-20) having a molecular weight of from 5,000 to 20,000 and a chlorine content of about 65%. Other film forming resins are polyester based polyurethanes having a molecular weight of about 20,000 and commercially available under the Trademark Desmodur RS.

The primer composition may also contain a catalytic effective amount of a catalyst which will catalyze the hydrolysis of silane when exposed to ambient moisture so that the silane will form a high strength bond with the glass or metal substrate. Such catalysts are known in the art and include catalysts which accelerate the reaction between isocyanates with compounds having an active hydrogen such as various tertiary amines but preferably compounds of heavy metals of Group I or Group II of the periodic table such as stannous octoate, stannous laurate and lead naphthenate. The amount of such a catalyst is not critical and may range from 0.1 weight % to 1 to 5 weight % based on the silane compound.

As noted, the silane based primers are known in the art and improve the adhesion of polyurethane polymers to glass and metals. In the installation of windshield sealants, the primer will be applied to the glass and the painted or partially painted car body. Sealant is then laid down on top of the primed car surface and the primed windshield pressed into place.

Both the primer and polyurethane sealant are placed in separate containers which are moisture-proof since both the primer and polyurethane sealant cure upon exposure to ambient moisture.

Reference is now made to the following Examples:-

Example 1

This Example uses only the organic tin curing catalyst and is for comparison purposes only.

The following components were used in this Example:

Compound	Parts by Weight
Polypropylene ether triol	100
Silica	25
Calcium Carbonate	30
Carbon Black	38
Diisodecyl phthalate (plasticiser)	30
Diphenyl methane diisocyanate	14.2
Dibutyl tin dilaurate	0.1
Diethyl malonate	2.3

The triol used in the above example was polypropylene ether triol having a molecular weight of about 6,500, commercially available under the Trademark Olin "Poly G 85-28".

A dry mixture (i.e. containing less than 0.06 weight % water) of the triol, fillers and plasticiser is prepared and the temperature of the mixture is adjusted to 48.8°C (120°F). The diisocyanate is then added to the mixture and this is followed by addition of the tin catalyst. When the exotherm reached 60°C (140°F) the diethyl malonate was added to stop the exotherm and block the remaining free isocyanate groups. The resulting composition had a viscosity of 450 poises.(at 25°C).

Example 2

This Example uses only the organic bismuth compound and is for comparison purposes only.

The following components were used in this Example:

Compound	Parts by Weight
Polypropylene ether triol'	100
Silica	25
Calcium Carbonate	30
Carbon Black	38
Diisodecyl phthalate	30

Diphenyl methane diisocyanate	14.2
Diethyl malonate	2.3
Bismuth tri-(2-ethyl hexoate) (8.2% Bi)	4.0

The organic bismuth compound was an 8.2 weight % solution, calculated as bismuth, in mineral spirits. The triol used in this example is the same polypropylene ether triol as used in Example 1. A dry mixture of triol, fillers and plasticiser is prepared, the temperature is adjusted to 48.8°C (120°F) and the diisocyanate is added to the mixture. The reaction mixture is heated at 60°C (140°F) until the reaction is complete. The diethyl malonate is then added followed by addition of the bismuth catalyst. The resulting composition has a viscosity of 480 poises (at 25°C).

Example 3

This Example demonstrates a polyurethane sealant in accordance with the present invention. The bismuth tri-(2-ethyl hexoate) is added as an 8.2 weight % solution, calculated as bismuth, in mineral spirits. The triol used is the same as in Examples 1 and 2.

The following components were used in this example:

Compound	Parts by Weight
Triol	100
Silica	25
Calcium Carbonate	30
Carbon Black	38
Plasticiser (didecyl phthalate)	32
Diphenyl methane Diisocyanate	14.2
Dibutyl Tin Dilaurate	0.1
Diethyl Malonate	2.3
Bismuth tri-(2-ethyl hexoate)	4.0

A dry mixture of the triol, fillers and plasticiser is prepared, the temperature of the mixture is adjusted to 48.8°C (120°F) and the diisocyanate and the tin salt are added. As in Example 1 when the exotherm reaches 60°C (140°F) the malonate is added and, after the reaction is complete, the bismuth catalyst is added. The resulting sealant has a viscosity of 450 poises (at 25°C).

Example 4

This is another Example of a polyurethane sealant of the present invention. The bismuth catalyst is identical to that used in Examples 2 and 3.

The following components were used:

Compounds	Parts by Weight
Tetrol (see below)	100
Silica	25
Calcium Carbonate	37
Carbon Black	35
Plasticiser (didecylphthalate)	30
Diphenyl Methane Diisocyanate	9.3
Dibutyl Tin Dilaurate	0.1
Diethyl Malonate	2.3
Bismuth tri-(2-ethyl hexoate)	4.0

The tetrol used in this example is polypropylene ether tetrol formed by reacting two moles of the triol of Example 1 with one mole of tolylene diisocyanate in the presence of a trace of dibutyl tin dilaurate (about 0.5% based on the weight of triol) and heating at 65.6°C (150°F) until no free-isocyanate is left. The resulting tetrol has a molecular weight of about 13,000 and a hydroxyl number of about 17. A dry mixture of tetrol, fillers and plasticiser is prepared, the temperature is adjusted to 48.8°C (120°F) and the diisocyanate is then added to the mixture. When the exotherm reaches 60°C (140°F) the diethyl malonate is added and when the reaction is completed the bismuth catalyst is

added. The resulting composition had a viscosity of 480 poises (at 25°C).

Example 5

The preferred silane base primer of the present invention uses the following components:

Compound	Parts by Weight
Ethyl Acetate	72
Carbon Black	7
Film Forming Resin (Desmodur RS)	12.5
2, 2, 4-trimethylhexamethylene Diisocyanate	0.8
Mercaptopropyl Trimethoxy Silane	3
Dibutyl Tin Dilaurate	0.2

The diisocyanate, silane and catalyst are charged into a reactor, the temperature is raised to 60°C (140°F) and the reaction allowed to proceed for from one to two hours. The temperature is then lowered to ambient and the remaining ingredients are added and mixed to form a homogeneous dispersion.

Example 6

In order to demonstrate the high tensile strength achieved in six hours by the polyurethane sealants of the present invention, particularly when compared to the strengths of the polyurethane composition of Examples 1 and 2, the following tests were conducted:

The primer of Example 5 was applied to four glass panels approximately 10.16cm x 10.16cm (4" x 4") in a strip along the sides of each panel approximately 2.54cm (one inch) wide. Thereafter, each of the polyurethane compositions of Examples 1, 2, 3 and 4 were laid, respectively, on the primer and on top of the polyurethane compositions was embedded a painted metal strip 12.7cm (1/2 inch) wide and 10.16cm (4 inches) long. After six hours the metal strips were torn off to measure the tensile strength of the bond.

The tensile strengths were as follows: Example 1, 3.51 kg/cm^2 (50 psi); Example 2, 2.11 kg/cm^2 (30 psi); Example 3, 7.03 kg/cm^2 (100 psi); and Example 4, 8.43 kg/cm^2 (120 psi).

In order to demonstrate the ultimate elongation of the compositions of Examples 3 and 4 they were allowed to remain in place for twenty-one days, after they were initially mixed and after standing in moisture-proof containers for three months. The tests were conducted in accordance with ASTM D 412-75 and the results are given in the following table:

	Initial		3 Months	
	Ex.3	Ex.4	Ex.3	Ex.4
Ultimate Elongation	700%	650%	750%	600%

CLAIMS

1. A polyurethane sealant which when exposed to ambient moisture will cure rapidly to form a seal having high tensile strength, comprising:

(A) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of the polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane polymer being the reaction product of (1) a liquid poly (lower)alkylene ether polyol having a molecular weight of greater than about 6,000 and from three to five hydroxyl groups with (2) a sterically unhindered aromatic diisocyanate;

(B) a catalytic curing effective amount of a curing catalyst;

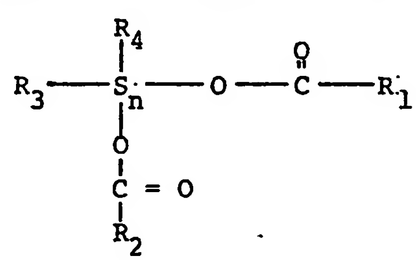
(C) up to 200 weight percent, based on the weight of the polyol, of inert fillers; and

(D) up to 100 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers,

characterised in that the curing catalyst comprises:

(a) an organic bismuth salt selected from bismuth tri-(2-ethyl hexoate) and bismuth tri-(neo-decanoate); and

(b) an organic tin compound of the formula



wherein R_1 and R_2 are the same or different and each is an alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl group.

2. A polyurethane sealant as claimed in Claim 1 characterised in that the liquid polyol has a molecular weight of from about 6,000 to about 30,000.

3. A polyurethane sealant as claimed in Claim 1 or Claim 2 characterised in that the organic bismuth compound is present in an amount of from about 0.1 weight percent to about 0.6 weight percent, calculated as bismuth and based on the weight of the polyol.

4. A polyurethane sealant as claimed in any of Claims 1 to 3 characterised in that the organic tin compound is present in an amount of from about 0.1 weight percent to about 1 weight percent based on the weight of the polyol.

5. A polyurethane sealant as claimed in any of Claims 1 to 4 characterised in that the organic tin compound is dibutyl tin dilaurate.

6. A polyurethane sealant system which when exposed to ambient moisture will cure rapidly to form a seal having high tensile strength, including:

(A) a liquid polyurethane sealant comprising:

(1) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of the polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane polymer being the reaction product of:

(i) a liquid poly(lower)alkylene ether polyol having a molecular weight of greater than 6,000 and from 3 to 5 hydroxyl groups with

(ii) a sterically unhindered diisocyanate;

(2) a catalytic curing effective amount of a curing catalyst;

(3) up to 200 weight percent, based on the weight of the polyol, of inert fillers;

(4) up to 50 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers; and

(B) a silane based primer composition which is rapidly curable in the presence of ambient moisture and comprising:

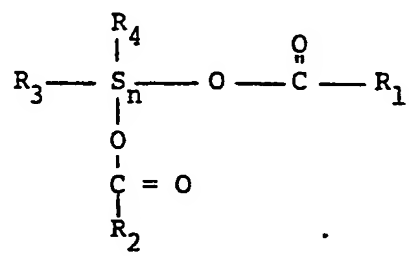
(I) a silane compound having isocyanate reactive groups; and

(II) a catalytic effective amount of a silane hydrolysis catalyst;

characterised in that the polyurethane curing catalyst comprises:

(a) an organic bismuth salt selected from bismuth tri-(2-ethyl hexoate) and bismuth tri-(neo-decanoate); and

(b) an organic tin compound having the formula



wherein R_1 and R_2 are the same or different and each is an alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is the lower alkyl group.

7. A polyurethane sealant system as claimed in Claim 6 characterised in that the volatile blocking agent is a tautomeric enol or a di(lower)alkyl malonate.

8. A method of forming a high tensile strength seal on a glass substrate which comprises priming the glass substrate which is exposed to ambient moisture with

(A) a silane based primer composition which is rapidly curable in the presence of ambient moisture and including:

(1) a silane compound having isocyanate reactive groups; and

(2) a catalytic effective amount of a silane hydrolysis catalyst; and then applying over said silane

base primer

(B) a liquid polyurethane sealant comprising

(i) a polyurethane polymer containing terminal isocyanate groups in an amount of not more than about 2.0 weight percent based on the weight of said polyurethane, the terminal isocyanate groups being blocked to prevent further reaction by a volatile blocking agent, said polyurethane being the reaction product of:

(a) a liquid poly(lower)alkylene ether polyol having three to five hydroxyl groups and a molecular weight of greater than about 6,000; and

(b) a sterically unhindered aromatic diisocyanate;

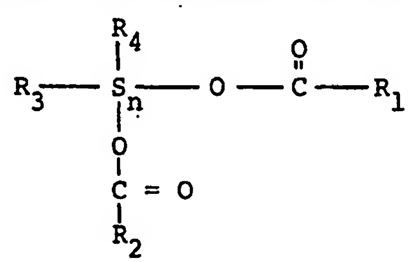
(ii) a catalytic curing effective amount of a curing catalyst;

(iii) up to 200 weight percent, based on the weight of the polyol of inert filler; and

(iv) up to 50 weight percent, based on the weight of the polyol, of polyurethane compatible plasticisers, characterised in that the curing catalyst comprises:

(I) an organic bismuth compound selected from bismuth tri-(2-ethyl hexoate) and bismuth tri- neo-decanoate ; and

(II) an organic tin compound of the formula



wherein R_1 and R_2 are the same or different and each is a lower alkyl group having from 1 to 12 carbon atoms and R_3 and R_4 are the same or different and each is a lower alkyl group.

9. A method as claimed in Claim 8 characterised in that the poly(lower)alkylene ether polyol is a polypropylene ether polyol.

10. A method as claimed in Claim 8 or Claim 9 characterised in that the silane hydrolysis catalyst promotes the reaction of an isocyanate with an active hydrogen and in that the catalyst is a compound of a heavy metal of Group I or Group II of the periodic table.